

Superconductivity in Fullerene Systems

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Abstract. Using the "standard model" for calculating electronic structure and BCS theory as a basic theoretical framework, some results, predictions, discussions, and speculations are presented related to superconductivity in C_{60} , C_{36} , and $C_{24}N_{12}$ molecular solids, $B_xC_yN_z$ nanotubes, and peapods. For gated C_{36} superconductors, it is suggested that higher levels of doping will cause superconductivity in other subbands.

INTRODUCTION

The discovery [1] of superconductivity in 1911 has had an enormous influence on science. In addition to the practical applications for technology, the fields of theoretical physics and of materials synthesis and characterization owe much to investigations of superconductivity and the search for superconducting materials. One of the most active subareas of this field is the search for higher superconducting transition temperatures. Although theoretical considerations have been useful, success in this field is primarily due to experimental searches guided by insight and in some cases methodical testing. The maximum transition temperature T_c^{\max} had only increased by 20K to around 25K in the 75 years since the discovery of superconductivity when the 1986 breakthrough on copper oxide materials by Bednorz and Müller [2] occurred. At this point, their work has led to an increase in the transition temperature for oxide materials from less than 1K [3] in $SrTiO_3$ to around 165K for Hg-Ba-Ca-Cu-O materials under pressure [4].

The discovery and identification [5] of C_{60} molecules and of the carbon nanotube [6] resulted in a broad spectrum of research. For superconductivity, as in the case of the oxides, T_c^{\max} was raised from less than 1K for intercalated graphite to the 30–40K range [7] in chemically doped C_{60} systems and to 52K for charges introduced through gated geometries [8]. Nanotube superconductivity has been predicted [9] and there are recent experimental results [10] for small diameter carbon nanotubes.

Although there is no consensus on the underlying theory and mechanisms for superconductivity in the copper oxide superconductors, it will be argued here that the properties of fullerene superconductors such as the C_{60} based materials and carbon nanotubes are, in the main, explainable using the "Standard Model" for electronic structure [11] and BCS theory [12] with electron-phonon induced pairing. This latter

statement is probably also correct for oxide superconductors without Cu such as $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ and the newly discovered MgB_2 [13].

If one accepts the arguments for a BCS electron-phonon induced pairing model for C_{60} and carbon nanotubes, then speculations [14] about obtaining even higher T_c 's for C_{36} and $\text{C}_{36-x}\text{N}_x$ based systems or superconductivity in doped BN nanotubes [15,16] should be taken seriously. Although detailed calculations for the BN nanotubes have not been presented, similar arguments to those made for carbon nanotubes are appropriate.

The Standard Model and BCS Theory

For a broad class of solids and clusters having itinerant electrons it is possible to explain and predict their electronic and structural properties. Techniques such as the plane-wave pseudopotential approach together with density functional theory constitute a scheme or standard model [11] which is applicable when electron correlation is not too large. This approach also allows the calculation of electronic, structural, vibrational, and electron-lattice coupling properties for use with the BCS theory of superconductivity [12] to predict and explain properties of superconductors [11].

Because electron correlation is moderately large in fcc C_{60} solids and in A_xC_{60} where A is an alkali atom, the question of whether the standard model and BCS theory are appropriate descriptions was called into question. However, calculations of the electronic structure [17,18] electron-phonon matrix elements [19], and transport calculations [20] give a consistent picture of these properties and the measurements of the normal and superconducting properties. It can be argued that for A_3C_{60} and for a C_{60} crystal with electrons or holes induced through external gates that the picture of C_{60} molecules emersed in a sea of fairly itinerant electrons is appropriate. Using the standard model and the view that electron pairing is achieved through intermolecular phonon excitations leads to a theoretical picture consistent with the experimental observations.

The input to the BCS theory are the phonon frequencies ω , the electron-phonon coupling parameter λ or λ^* where $\lambda^* = \frac{\lambda}{1+\lambda}$, and the Coulomb repulsion parameter

μ or $\mu^* = \frac{\mu}{1 + \mu \ln \frac{\omega_{\text{ph}}}{E_F}}$ where E_F is the Fermi energy and ω_{ph} is an appropriate

phonon cutoff frequency. Using the standard model, λ can be calculated from a sum over the Fermi surface of the electron-phonon matrix element $M_{kk'}$ for scattering an electron from state k to k' with associate energies ϵ_k and $\epsilon_{k'}$;

$$\lambda = \frac{\sum_{\mathbf{k}, \mathbf{k}'} \frac{|M_{\mathbf{k}\mathbf{k}'}|^2}{\hbar \omega_{\mathbf{k}-\mathbf{k}'}} \delta(\epsilon_{\mathbf{k}}) \delta(\epsilon_{\mathbf{k}'})}{\sum_{\mathbf{k}} \delta(\epsilon_{\mathbf{k}})} \quad (1)$$

where $\omega_{\mathbf{k}-\mathbf{k}'}$ is the phonon frequency involved in the scattering. Equation (1) can be used to compute λ , but an alternate form is more useful for discussing λ physically

$$\lambda \sim \frac{N(E_F) \langle I^2 \rangle}{M \langle \omega^2 \rangle} \quad (2)$$

where $\langle I^2 \rangle$ is the Fermi surface average of the square of the displacement induced electron scattering matrix element, M is the atomic mass, $\langle \omega^2 \rangle$ is an average of the square of the phonon frequencies, and $N(E_F)$ is the electronic density of states at E_F . Equation (2) can be described as the ratio of an electronic spring constant and a phonon spring constant. Hence for harmonic systems λ is a dimensionless coupling constant which is independent of M and increases when the electronic spring constant becomes stiffer and the lattice is "softer".

The modern theory of T_c for conventional superconductors is based on Eliashberg theory [21]. Approximate analytic expressions exist for moderate λ such as the McMillan Equation [22]

$$T_c = \frac{\hbar \omega_{\log}}{1.2 k_B} \exp \left[\frac{-1.04(1+\lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*} \right] \quad (3)$$

where ω_{\log} is an appropriate average of the phonon frequencies, and k_B is Boltzmann's constant. The McMillan equation for $T_c(\lambda)$ saturates for large λ whereas numerical solutions of the Eliashberg equation lead to a $\sqrt{\lambda}$ dependence for large λ . Although simple analytic expressions for $T_c(\lambda, \mu^*)$ over a wide range of λ are not available, it is possible to obtain an expression for the case where $\mu^*=0$. The Kresin-Barbee-Cohen form [23,24]

$$T_c = 0.25 \frac{\sqrt{\omega^2}}{\sqrt{e^{\frac{2}{\lambda}} - 1}} \quad (4)$$

is exponential for small λ and has the correct $\sqrt{\lambda}$ behavior at large λ . The quantity $\sqrt{\langle \omega^2 \rangle}$ is an average of the phonon frequencies.

Another useful parameter to use as input to the theory is the isotope effect parameter α where $T_c \propto M^{-\alpha}$ for ionic mass M . In the simplest McMillan type model

$$T_c \sim \omega_{ph} e^{-\frac{1}{\lambda^* - \mu^*}} \text{ and} \quad (5)$$

$$\alpha = \frac{1}{2} \left[1 - \left(\frac{\mu^*}{\lambda^* - \mu^*} \right)^2 \right]. \quad (6)$$

The C_{60} Superconductors

Using the above as a theoretical basis, the experimental data on the normal transport properties [20] and the superconducting properties are consistent with a phonon induced pairing model for the superconductivity where the dominant phonons are intramolecular in nature. The measurements of T_c and α support this description. For example [25], using Rb_3C_{60} as a prototype, $\alpha_{Rb} \approx 0$ indicating that the Rb vibrations are not important for the phonon mechanism, while $\alpha_C \approx 0.2$ is consistent with reasonable values for the parameters λ , μ^* , and the average phonon frequencies [25]. In addition, photoemission spectra [26] yield a superconducting gap Δ to T_c ratio for Rb_3C_{60} of $\frac{2\Delta}{k_B T_c} = 3.53$ which is consistent with BCS theory.

Similar results are obtained for K_3C_{60} .

Recently both electron and hole doping has been achieved using gated geometries [8]. In this study the maximum T_c found for electron doping of a C_{60} layer is 11K while hole doping yields values of T_c up to 52K. Because of the dependence of λ on the density of states $N(E_F)$ in Eq. (2), it is reasonable to investigate whether the dependence of T_c on doping is directly associated with changes in $N(E_F)$. For A_3C_{60} systems it has been demonstrated that larger lattice constants yield higher T_c 's. This has been interpreted in terms of monotonic increases in $N(E_F)$ with lattice constant since $N(E_F)$ is inversely related to the bandwidth which in turn is inversely related to the lattice constant. The measured negative dependence of T_c on pressure is supportive of this idea. However it should be pointed out that peaks in the density of states do not necessarily imply large increases in T_c . This point can be illustrated using a total dielectric function model to evaluate the pairing interactions where both the attractive and repulsive contributions to the pairing are included. Then the argument can be made using a BCS model for illustration. The "NV" BCS parameter representing the density of states times the pairing potential is inversely related to the dielectric function which itself is roughly proportional to N for large N . Hence peaks in the density of states tend to cancel out.

For systems such as the C_{60} based materials the argument is not operative using the current model [27] for the superconductivity where N is determined by the band structure and carriers from alkali atoms or other doping whereas V is dominated by intramolecular vibrations. This separation is consistent with the lattice constant and pressure dependence of T_c and it results in a more straightforward dependence of T_c on $N(E_F)$ arising from the dependence of λ on $N(E_F)$.

If we examine the electronic structure of C_{60} for the fcc [18] structure, the supporting photoemission results [28] and the further theoretical studies [29] of the density of states for the Fm3, Pa3 and isotropically, merohedrally disordered structures, characteristic peak structures in the density of states are evident. In particular the H_u states for the holes (HOMO) has a two-peak structure each having a width of about 0.5eV. For the electron states the T_{1u} , (LUMO) state also has a two peak structure with similar widths. It is not clear at this point how to line up the charge per C_{60} molecule axis (CPM) of figure 4 of ref. 8 with the energy scale of the density of states. However, instead of assuming [8] that the peak in T_c for the hole doping case plotted against CPM mimics the entire density of states for the H_u band, here we suggest that this peak in T_c is associated with only the first or highest energy HOMO peak. This interpretation also predicts that further doping could push the Fermi level through the valley between the peaks and then T_c could rise again. The electronic structure calculations suggest that the next peak is higher than the first, and this could result in a high T_c .

It is important to note that the coupling of the phonons to the holes in the H_u band changes as E_F moves through the band. This originates from the changes in the character of the electronic states at each \bar{k} -point in the band and also from their coupling to the phonons for different wavevectors \bar{q} . In addition, as the density of states gets lower, correlation effects play a larger role. At this time, we do not have access to data on the temperature dependent resistivity for different doping levels so these are open questions. The tendency toward a metal-insulator transition would decrease T_c for the lower density of states regions resulting in a faster rise and decline in T_c as a function of doping than one obtains with just an Eliashberg calculation of T_c assuming a robust metallic system. Also the two peaked structure may not be evident in T_c (CPM) if correlation effects are strong.

Similar considerations to those presented above for hole doping would be operative for electron doping. Here the T_{1u} band is of interest and the lower T_c arises because of the lower values for $N(E_F)$ or electron-phonon coupling in this band.

Using a Lorentzian density of states and a six electron or hole maximum with λ proportional to the density of states, we have performed an Eliashberg calculation with $\omega_{\log} = 1200K$ and μ^* used as a parameter to refine the fit to the data. For the electrons, the peak maximum $T_c = 10K$ while the maximum T_c for the holes = 47K. The variation in μ^* used is small and within the accepted values for these systems. As discussed above, this calculation suggests another peak in T_c for both electron and hole doping when the doping level is increased.

Higher T_c 's?

As stated in the last section, the rise in T_c from below 1K for graphite to the 50K range for C_{60} is similar to what occurred for the oxide superconductors from $SrTiO_3$ to $La_{2-x}Ba_xCuO_4$. There is, of course, considerable motivation to attempt to mimic the next rise found in the oxides to T_c 's above the boiling point of liquid nitrogen and beyond. Another goal is to continue the exploration of the study of these materials systems to find more novel superconductors.

One natural extension of the current studies is to explore methods of increasing $N(E_F)$. For the gated C_{60} systems, doping into other peaks in the density of states is desirable. Also, increasing the lattice constant of the C_{60} layer may lead to larger T_c 's as in the case of the A_3C_{60} systems. Besides doping into regions of higher density of states, increasing the density of states of the system by introducing different electronic character is an option. A good example is the work of Umemoto and Saito[30] on Ba_4C_{60} where the d-electron states of Ba can lead to higher $N(E_F)$ and hence higher T_c 's.

Another path to higher T_c 's for fullerene-like systems is to maximize the coupling of the electrons to the phonons. The T_c increase in going from graphite to the C_{60} systems is believed to result from the increase in the number of electron-phonon coupling channels. For graphite, the π orbitals with p_z character do not couple to s-like orbitals for various displacements. When curvature is introduced as in the case of C_{60} systems, this breaks the mirror symmetry and mixes the p_z and s orbitals which leads to a fivefold increase in the coupling.

A similar curvature argument can be made for evaluating the couplings for the case of nanotubes [9] and smaller fullerene molecules such as C_{36} and $C_{24}N_{12}$ [14,31,32]. An approximate expression for the electron-phonon pairing potential can be written [9] in terms of a flat component appropriate for graphite and a curved contribution which scales with the square of the radius of curvature. Many aspects of the results of the first-principles calculations can be recovered using this simple model for the decomposition of the pairing potential. For example, in the nanotube case T_c can be evaluated [9] as a function of tube radius. For large radii, the T_c curve approaches values appropriate for graphite while T_c increases rapidly as the radius is reduced. For very small radii, T_c increases dramatically. The results are consistent with the recent reports [10] of superconductivity in very small tubes $\sim 4 \text{ \AA}$.

In general, there is good agreement between several authors on the first principles calculation of the electron-phonon coupling strength for C_{60} and its fivefold increase from graphite [19]. Hence the application of this approach to the case of C_{36} should have credibility. An important caveat is the fact that crystal structure can play an important role, and at this point a solid C_{36} sample of known structure is not available. However, for the structures studied, a comparison of T_c for solid C_{36} with that of K_3C_{60} predicts a sixfold increase in T_c which would suggest superconductivity at temperatures above the boiling point of nitrogen [14]. An interesting companion compound is $C_{24}N_{12}$ which in addition to having the increased curvature of C_{36} over C_{60} , there are added positive features arising from the chemical changes such as changes in bond lengths.

The recent synthesis [33] of peapods (C_{60} molecules in carbon nanotubes) suggest interesting modifications of the C_{60} density of states and hence T_c . These effects are likely to be even more dramatic in C_{36} peapods if they are fabricated.

Hence modifications of the density of states and the electron-phonon couplings appear to be possible in fullerene systems through geometric and chemical changes. $B_xC_yN_z$ tubes and molecules with chemical or gated dopings in films or peapods or other geometric configurations may lead to higher T_c 's. In any case, the search should prove to be scientifically interesting.

ACKNOWLEDGMENTS

I would like to thank Professor Vincent H. Crespi for calculating the Eliashberg solutions for T_c on C_{60} reported here. This work was supported by National Science Foundation Grant No. DMR00-87088 and by the Director, Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy under Contract DE-AC03-76F0098.

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